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On the vibrational spectra of benzyl benzoate

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[Plate 6]

Raman and infrared spectra of benzyl benzoate have been studied and the observed results have been compared to those reported for similar double molecules by previous authors. The results indicate that the two phenyl rings may be reasonably assumed to be only weakly coupled and their vibrations may be treated separately. In characterizing the phenyl ring vibrational frequencies, assignments reported for suitable monosubstituted benzene molecules have been duly considered for comparison. Tentative assignments for vibrations of the substituent group have also been made.

Introduction

In recent times several authors have reported analysis of vibrational spectra of a class of molecules containing two benzene rings connected through a weakly conjugated linkage, some times called "double-molecules". From a study of the infrared spectra of diphenyl and its derivatives Cannon & Sutherland (1951) concluded that in such molecules the two benzene rings vibrate independently. Steele & Lippincott (1961) discussed the close resemblance of the vibrational spectra of diphenyl and deca-deutero-diphenyl with the spectra of monosubstituted benzenes and assigned the frequencies of these compounds to different modes by comparing the data with those of fluoro-benzene. Katon *et al* (1964) observed that the two benzene rings of diphenyl ether are not equivalent and the benzene like vibrations of the molecule could be treated in terms of a monosubstituted benzene In their infrared absorption study, some of the bands due to phenyl ring vibrations were found to occur in pairs. Recently, Green (1968) reported vibrational assignments for the 'double-molecules' diphenyl ether and diphenyl sulphide.

The molecule of benzyl benzoate may also be treated as a 'double molecule' in which the two benzene rings are connected through the $-\overset{\overset{O}{\|}}{C}-O-CH_2$ group. The vibrational spectrum of this molecule has not been analysed before and it would be of interest to find out whether the spectrum exhibits the characteristics of a double-molecule. For this purpose a study of the Raman spectrum of benzyl benzoate in the liquid state and the infrared spectra of the compound in the liquid state and in solutions was made. In this paper the results and their analysis have been presented.

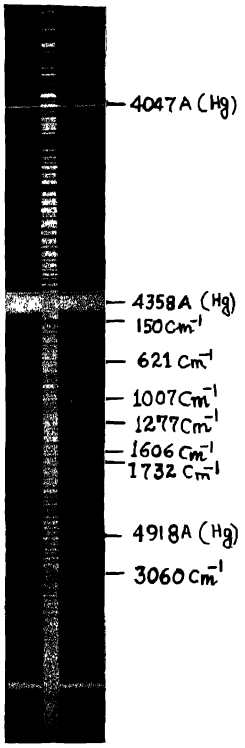

Figure 1. Raman spectra of benzyl benzoate (Pure liquid at 28°C)

Experimental

Sample of pure benzyl benzoate was supplied by Rhodia (France) and was first fractionally distilled and the proper fraction thus collected was repeatedly distilled under reduced pressure before use.

The Raman spectrum and the state of polarisation of the Raman lines were recorded in a manner described in a previous paper (Chattopadhyay & Mukherjee 1967). The infrared spectra of the sample in the liquid state and in solutions in different solvents were recorded in the usual way with a Perkin-Elmer Model 21 spectrophotometer fitted with NaCl optics. The measured frequencies are accurate within ± 5 cm^{-1} for broad band near 3000 cm^{-1} region below which the accuracy is still higher ($\sim \pm 2$ cm^{-1}). All measurements were made at 26°C.

Results

The Raman spectrum and the infrared absorption curves of the sample are reproduced in figures 1 (plate 6) and 2 respectively. The Raman shifts ($\Delta\nu$ cm^{-1}) and infrared absorption frequencies (ν cm^{-1}) of benzyl benzoate in liquid state and in solutions in CCl_4 and $CHCl_3$ together with their intensities and observed state of polarisation of the Raman lines are included in table 1. The assignments of the freqencies to vibrational modes of the ring and the internal vibrations of the substituent group are summarised in tables 2 and 3 respectively.

Discussion

The molecule of benzyl benzoate should normally belong to the point group C_1 and its seventy eight normal vibrations should all be active both in Raman effet and in infrared absorption. These will include eighteen vibrational modes of the substituent group some of which may be identified with some certainty while the remaining sixty vibrations should be characteristic of the two benzene rings. But it can be seen from table 1 that the number of observed frequencies in the vibrational spectrum of benzyl benzoate is much smaller than the total number of sixty expected ring vibrations even though some of the vibrational bands in the infrared absorption spectrum (figure 2) are found to occur in pairs. These results are similar to those observed for diphenyl ether (Katon *et al* 1964) and diphenyl sulphide (Green 1968). Assignment of the observed vibrational frequencies to different modes of vibration of the molecules has been proposed and an attempt has been made to understand the characteristic feature of the infrared spectrum. Discussions have been presented in the following paragraphs.

TABLE 1

Raman shifts ($\Delta\nu$ cm^{-1}) Liquid at 28°C	Infrared frequencies (ν cm^{-1})		
	Pure liquid at 26°C (Thin film)	Solution in	
		CCl_4	$CHCl_3$
150 (1) D			
205 (3b) D ?			
249 (2)			
621 (5) D	628 sh		625 vw
680 (1)	675 s	676 m	674 s
	686 sh	686 vs	685 sh
	705 vsb		710 sh
	720 sh	720 s	725 sh
	735 vs		
	745 vs		
807 (3)	804 s		798 sh
825 (1)	825 m	830 vw	832 sh
	845 m	850 sh	850 m
901 (2) P	888 m	885 m	
	916 vs	912 m	915 m
964 (0)	962 vsb	958 wb	963 w
1007 (10) P	1003 s	1006 vw	1005 sh
1034 (4) P	1026 vs	1030 vs	1030 vs
	1070 vs	1072 vs	1072 vs
	1106 vsb	1112 vs	1115 vs
1162 (4) D	1160 s	1162 vvw	
1182 (2) P	1179 vs	1178 s	1180 s
1216 (3) P	1216 vs	1216 w	1220 vsb
	1254 vs	1255 sh	1255 sh
1277 (4b) D	1265 vs	1272 vsb	1275 vs
1320 (0)	1316 vs	1318 s	1318 s
1385 (3) P	1380 vs	1382 m	1382 m
	1430 sh	1426 w	1428 mb
1459 (1)	1455 vs	1458 s	1456 s
	1500 vs	1502 w	1504 m
1606 (8b) D	1606 vs	1606 m	1605 m
1732 (6b) P	1720 vsb	1725 vs	1720 vs
	2880 mb	2900 w	
	2966 s	2970 wb	2970 sh
	3030 sh		3045 s
	3058 vs		
3060 (6b) P	3063 vsb	3060 m	

TABLE 2. ASSIGNMENTS OF THE PHENYL RING VIBRATIONS

Nature of the mode	Correspondence with vibration no. in benzene (Pitzer & Scott, 1943)	Ring I	Ring II	Methyl benzoate	Benzyl acetate
		(Vibrational frequencies in cm^{-1})			
a^a					
ν(CH)	20A	3063	3063		3080
ν(CH)	20B	3063	3063		3080
ν(CH)	7B	3058	3058	3073	3067
ν(CH)	2	3030	3030	3073	3037
ν(CH)	13	3030	3030	3073	3045
ν(CC)	8B	1606	1606	1603	1605
ν(CC)	8A	1606	1606	1591	1590
ν(CC)	19A	1500	1500	1495	1499
ν(CC)	19B	1455	1455	1452	1485
ν(CC)	14	1380	1380	1376	1380
β(CH)	3	1316	1316	1311	1362
β(CH)	9A	1179	1179	1183	1180
β(CH)	9B	1160	1160	1160	1160
β(CH)	15	1106	1070	1064	1040
β(CH)	18A	1034	1026	1028	1025
Ring breathing	1	1003	1003	1003	1000
α(CCC)	6B	621	628	621	620
X-sensitive	7A	1216	1216	1111	1214
X-sensitive	12	825	845	826	830
X-sensitive	6A	249	249	360	482
X-sensitive	18B	205	205	218	367
a''					
γ(CH)	5	962	962	969	960
γ(CH)	17A	916	888	938	915
γ(CH)	10A	804	804	850	830
γ(CH)	11	735	745	710	740
γ(CH)	17B	705	720	686	692
ϕ(CC)	4	686	675	679	640
ϕ(CC)	16A				400
X-sensitive	16B				254
X-sensitive	10B	150	150	134	178

TABLE 3. ASSIGNMENTS OF INTERNAL VIBRATIONS OF SUBSTITUENT GROUP

Approximate nature of the modes	Vibrational frequencies (in cm^{-1})
CH_2 asymmetric stretching	2966
CH_2 symmetric stretching	2880
C = 0 stretching	1720
CH_2 scissoring	1430
C – 0 stretching	1265
CH_2 wagging	1254

(a) *Vibrations of the phenyl ring*

It can be seen from table 1 that the observed vibrational spectra of benzyl benzoate contain a large number of frequencies whose values are almost identical with those of many monosubstituted benzene compounds. So, for the purpose of assignment of these vibrational frequencies the molecule of benzyl benzoate (ϕ_I $COOCH_2$ ϕ_{II}) has been treated as monosubstituted benzene in two different ways. In one case the molecule is looked upon as a benzoic acid ester ϕ_I $C(=O)OX$ where X represents $CH_2\phi_{II}$ and in the other, it is treated as a benzyl derivative ϕ_{II} CH_2X, X representing the group ϕ_I $C(=O)O$. With these assumptions, qualitative comparison of the frequencies of vibrations involving mainly the ring ϕ_I of benzyl benzoate molecule has been made with those of methyl benzoate, while in the case of the ring ϕ_{II} comparison with benzyl derivative like benzyl acetate has been made. The frequencies due to methyl benzoate (Chattopadhyay 1968) and benzyl acetate have been included in table 2 for this purpose. In view of some recent work it was found necessary to revise the assignments of some of the frequencies for benzyl acetate reported earlier by Chattopadhyay *et al* (1967) and for the sake of consistency the revised assignments have been included in the table. In analysing the observed vibrational bands of benzyl benzoate molecule, it has been found convenient to assume the symmetry of the molecule to be at least approximately C_i with the two rings either in the same plane or oriented through an angle of 90° with respect to each other. Moreover, in order to account for the intensities of some of the bands in the Raman and in infrared

spectra and the polarisation of Raman lines, the local symmetry of each ring, which is C_{2v}, was found to be an important determining factor.

The assumption that the molecule of benzyl benzoate may be treated as a monosubstituted benzene in two ways is equivalent to assuming that the two rings may be treated independently. Since this implies that they may be considered to be only weakly coupled such that the corresponding vibrations of the two rings are almost noninteracting some of the modes of vibrations of one ring, especially those not sensitive to substitution should be expected to have frequencies only slightly different from the frequencies due to corresponding modes of the other ring. But it is seen from table 1 that such doubling of vibrational frequencies does not occur in most cases which leads to the conclusion that the vibrational frequencies due to many of the modes of one ring are indentical with those of the corresponding modes of the other ring. On the basis of the assignments proposed in table 2 it is seen that these frequencies correspond to the modes which are least affected by substitution. Similar conclusions were previously arrived at by Katon *et al* (1964) for diphenyl ether molecule. It is, however, seen (figure 2) that some of the vibrational frequencies arising from such modes appear as pairs of infrared bands and according to the assignments given in table 2, most of these correspond to the modes of benzene which involve in-plane and out-of-plane bending vibrations. Due to limitation of the rock salt optics in the infrared spectrophotometer used, only two modes among the six substituent-senstive low frequency vibrational modes which are expected to exhibit more pronounced doublet character, could be studied in the infrared. Of these two modes, one mode corresponding to the substituent-sensitive mode 12 (Pitzer & Scott 1943) is observed to give two distinct frequencies at 825 and 845 cm^{-1} (figure 2, table 2).

(b) *Internal vibrations in the substituent group*

Of the frequencies originating from the internal vibrations of the substituent group, the infrared absorption bands at 1720, 2880 and 2966 cm^{-1} may be readily assigned to C = O stretching, CH_2 symmetric stretching and CH_2 asymmetric stretching modes respectively. There is a broad and strong Raman line at 1277 cm^{-1}, whereas the infred absorption curves clearly show two resolved bands at 1254 and 1265 cm^{-1}. These two infrared bands have been assigned to CH_2 wagging and C – O stretching modes respectively. The frequency due to CH_2 scissoring mode is generally expected in the 1450 cm^{-1} region. As such, the band at 1430 cm^{-1} which appears as a shoulder in the infrared spectrum is tentatively assigned to this mode.

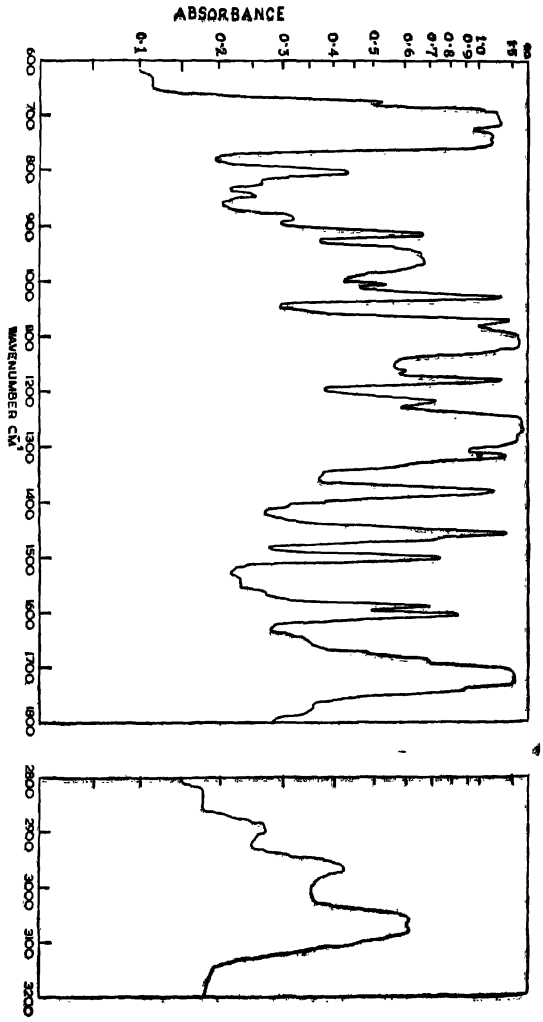

Figure 2. Infrared spectra of benzyl benzoate (liquid, thin film, at 26°C).

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